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Inelastic neutron scattering study of the hydration of tricalcium silicate

S.A. FitzGerald, D.A. Neumann, J.J. Rush, R.J. Kirkpatrick, X. Cong, R.A. Livingston

ABSTRACTS**COMMUNICATIONS****Transformation probability of graphite-diamond assisted by nonmetallic catalysts at high pressure and high temperature**L. Sun,* Q. Wu,* Y. Zhang,* W. Wang*
(*Chinese Academy of Sciences, †Lanzhou University)

The tendency of graphite-diamond transformation assisted by non-metallic catalysts of carbonates, sulfates, or phosphorus under high pressure and high temperature has been investigated by calculating the activation energy and transformation probability of the carbon atoms over a potential barrier. It was found that the activation energy is highly sensitive to the catalyst chosen. The value of activation energy in the systems of graphite-carbonates, graphite-phosphorus, and graphite-sulfate are 130.71×10^3 J/mol, 206.03×10^3 J/mol, and 221×10^3 J/mol, respectively. If f_d stands for the probability of the transformation from graphite to diamond, the probability sequence of graphite-diamond transformation in different systems was put forward:

$$f_{d(\text{gr-carbonate})} > f_{d(\text{gr-phosphorous})} > f_{d(\text{gr-sulfite})}$$

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Highly (200)-oriented Pt films on SiO₂/Si substrates by seed selection through amorphization and controlled grain growth

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(*Seoul National University, †Tong Yang Central Laboratories)

Highly (200)-oriented Pt films on SiO₂/Si substrates were successfully prepared by combination of a dc magnetron sputtering using Ar/O₂ gas mixtures and subsequent controlled annealing. The intensity ratio of (200) to (111) planes (I_{200}/I_{111}) was over 200. The (200)-oriented Pt microcrystallites were less susceptible to amorphization due to their lower strain energy with oxygen incorporation than (111)-oriented ones. The controlled grain growth from the selected (200)-oriented seed microcrystallites during subsequent annealing provided a kinetic pathway where grain growth of the seed microcrystallites was predominant, while suppressing the nucleation of surface energy-driven (111)-oriented seed microcrystallites and subsequent (111) preferred orientation.

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Local heating associated with crack tip plasticity in Zr–Ti–Ni–Cu–Be bulk amorphous metals

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(Stanford University)

Deformation in metallic glasses is generally considered to arise from flow in localized shear bands, where adiabatic heating is thought to reduce glass viscosity. Evidence has been inferred from the veined fracture surfaces and molten droplets reported for metallic glasses. In this work, the detailed spatially resolved surface temperature increase and subsequent dissipation

associated with crack tip plasticity in a Zr–Ti–Ni–Cu–Be bulk metallic glass is characterized for the first time. Maximum temperatures of up to 54.2 K were estimated from a heat conduction model and shown to be in excellent agreement with a nonhardening plasticity model for the heat generated by a propagating crack. Local cooling was also observed and shown to be consistent with thermoelastic effects.

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ARTICLES**Temperature and time dependence of phase formation of HgBa₂Ca_{n-1}Cu_nO_{2(n+1)+δ} (n = 1, 2, 3, 4) superconductors**A. Yamamoto, M. Itoh, A. Fukuoka, S. Adachi, H. Yamauchi, K. Tanabe
(International Superconductivity Technology Center)

We systematically studied the temperature and time dependence of phase formation of HgBa₂Ca_{n-1}Cu_nO_{2(n+1)+δ} (Hg-12(n-1)n, n = 1, 2, 3, 4) superconductors by a single-step firing method. All samples were synthesized from high-purity HgO, BaO, CaO, and CuO in a sealed quartz tube. The phase formation of Hg-12(n-1)n was examined by both x-ray diffraction (XRD) analysis and dc susceptibility measurement. A single-phase HgBa₂CuO_{4+δ} (Hg-1201) was obtained in a relatively wide temperature range (600–850 °C), while single-phase HgBa₂CaCu₂O_{6+δ} (Hg-1212) and HgBa₂Ca₂Cu₃O_{8+δ} (Hg-1223) were obtained only in narrow temperature and time ranges for the synthesis. The optimum temperatures for Hg-1212 and Hg-1223 were found to be 665 and 710 °C, respectively, when the sintering time was fixed for about 50 h. The HgBa₂Ca₃Cu₄O_{10+δ} (Hg-1234) phase was obtained as a mixture with Hg-1223.

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Thermal instability of (Bi,Pb)₂Sr₂Ca₂Cu₃O_x in contact with silver

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(Purdue University)

The chemical and microstructural evolution of particulate (Bi,Pb)2223 in contact with pure bulk silver at 830 to 905 °C under flowing air and Ar-5% O₂ atmospheres has been studied. Specimens annealed under PO₂ and temperature conditions for which the (Bi,Pb)2223 phase itself is stable, based on a critical assessment of the literature, revealed a silver/(Bi,Pb)2223 interface-limited reaction, producing both solid and liquid decomposition phases. The (Bi,Pb)2223 not in direct contact with silver exhibited no reaction under the same conditions. Solid silver dissolves into the (Bi,Pb)2223 incongruent liquid, facilitating the incongruent melting reaction. On cooling, equiaxed metallic silver particles precipitated uniformly throughout bulk specimens partially melted on a silver substrate.

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Fabrication and properties of arrays of superconducting nanowires

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We report on the fabrication and structural characterization of arrays of superconducting nanowires by electroplating lead into the nanopores of track-etched polymer membranes. The diameters of the lead nanowires range from 400 nm down to 70 nm, whereas their length is about 20 μm . Large enhancement of the critical field has been observed in good agreement with the Ginsburg-Landau-Silin theory. By comparing the predicted critical field enhancement for thin cylinders with experimental results, we have extracted the effective penetration depth. The dependence of the effective penetration depth and electron mean free path on the wire diameter is also discussed.

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Large grain polycrystalline silicon via chemical vapor deposition

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(Georgia Institute of Technology)

Large grain polycrystalline Si films were grown by chemical vapor deposition (CVD) onto TiB_2 substrates using the $\text{SiCl}_4\text{-H}_2$ reagent system. A statistically designed processing study was used to correlate the film growth rate, crystallographic orientation, and grain size with deposition temperature, the $\text{SiCl}_4 : \text{H}_2$ ratio, and the level of B doping. Each process variable influenced grain size, with temperature having the dominant effect. Grains as large as 15 to 20 μm were achieved for coating thickness of about 50 μm .

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Lattice-distortion-induced amorphization in indented [110] silicon

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High-resolution transmission electron microscopy (HRTEM) is used to reveal fine structures of amorphous silicon induced by Vickers indentation and its interface with unindented silicon matrix. Deformation microtwins at the interface and continuous transition from lattice structure of crystal into amorphous structure at the interface are observed. Within the amorphous silicon near the periphery of the indented region, there are many clusters characterized by distorted silicon lattice. A possible mechanism of lattice-distortion-induced amorphization at the periphery of indented silicon is suggested. All the indentations are performed at ambient temperature.

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Relating mechanical testing and microstructural features of polysilicon thin films

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(The Johns Hopkins University)

Polycrystalline silicon thin films (polysilicon) have been deposited on single crystalline silicon substrates, and square and rectangular windows have been etched into these substrates using standard micromachining techniques. Pressure-displacement curves of the resulting polysilicon membranes have been obtained for these geometries, and this data has been used to determine the elastic constants E and ν . The microstructural features of the films have been investigated by transmission electron microscopy (TEM) and x-ray diffraction. The grains were observed to be columnar and were found to have a $\langle 011 \rangle$ out-of-plane texture and a random in-plane grain orientation. A probabilistic model of the texture has been used to calculate the bounds of the elastic constants in the thin films. The results obtained from bulge testing ($E = 162 \pm 4$ GPa and $\nu = 0.20 \pm 0.03$) fall in the wide range of values previously reported for polysilicon and are in good agreement with the microsample tensile measurements conducted on films deposited in the same run as the present study (168 ± 2 GPa and 0.22 ± 0.01) and the calculated values of the in-plane moduli for $\langle 110 \rangle$ textured films ($E = 163.0\text{--}165.5$ GPa and $\nu = 0.221\text{--}0.239$).

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Spray pyrolysis preparation of porous polycrystalline thin films of titanium dioxide containing Li and Nb

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(University of Guelph)

Titanium dioxide thin films, prepared with and without lithium and niobium, were uniform, crack-free and stoichiometric, amorphous as-deposited at 300 $^\circ\text{C}$ and below, polycrystalline anatase when deposited at 400 $^\circ\text{C}$ or

annealed at 500–800 $^\circ\text{C}$, and rutile when annealed at 900 $^\circ\text{C}$. Films prepared around 200 $^\circ\text{C}$ were very porous, but the porosity decreased as the substrate temperature increased. Optical absorption spectra revealed an indirect band-gap of 3.0 eV for amorphous and anatase films, and a direct band gap of the same value in rutile. Dark dc conductivity of undoped films was lower than 10^{-10} ($\Omega \cdot \text{cm}$) $^{-1}$; Hall effect measurements indicated that effective electron mobility was below 1 $\text{cm}^2/(\text{V} \cdot \text{s})$. The presence of Nb and Li increased the conductivity by 2–3 orders of magnitude, similar to the effect of hydrogen annealing. Illumination increased the conductivity by several orders of magnitude, and the decay followed a multi-exponential law extending into the 10^6 s range after irradiation was stopped. The electronic properties of the films were determined by oxygen-related surface states at grain boundaries. Samples containing Li exhibited considerable sensitivity to water vapor.

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The effects of grain condition on magnetic properties in

$\text{Nd}_4\text{Fe}_{76}\text{Co}_3(\text{Hf}_{1-x}\text{Ga}_x)\text{B}_{16}$ alloy

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The best linear fit of $H_c(T)/M_s(T)$ versus $2k_1(T)/\mu_0 M_s^2(T)$ infers that H_c is determined by a nucleation process in nanocrystalline two-phase magnets. The condition of the grain shapes is improved after adding Hf and Ga, but the surfaces are deteriorated by some precipitates on the boundary. Taking into account the values of α , N_{eff} , the results of transmission electron microscopy (TEM), and Mössbauer spectroscopy, the magnetic field heat treatment not only induces grain refinement but also causes a uniform distribution of the soft and hard phases. Both the remanence and energy product values are increased by 20–30% for all ribbons after annealing with magnetic field. The magnetic interaction in $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B} + \alpha\text{Fe}$ -based nanocrystalline two-phase magnets is studied using δM plots in this paper. It is found that the exchange-coupled interaction is greatly enhanced in the sample annealed with magnetic heat treatment, especially $\text{Nd}_4\text{Fe}_{76}\text{Co}_3\text{Hf}_{0.5}\text{Ga}_{0.5}\text{B}_{16}$, which achieves the highest energy product $(\text{BH})_{\text{max}} = 15.8$ MGOe.

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Forging, textures, and deformation systems in a B2 FeAl alloy

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(University of Neuchâtel)

High-temperature forging experiments have been carried out by axial compression testing on a Fe-41Al-2Cr alloy in order to determine the deformation systems operating under such high-speed, high-temperature conditions and to examine the textures produced by such deformation and during subsequent annealing to recrystallize. Deformation is deduced to take place by the operation of $\langle 111 \rangle \{110\}$ and $\langle 111 \rangle \{112\}$ slip systems at low temperatures and by $\langle 100 \rangle \{001\}$ and $\langle 100 \rangle \{011\}$ slip systems at high temperatures, with the formation of the expected strong $\langle 111 \rangle$ textures. The examination of the weak $\langle 100 \rangle$ texture component is critical to distinguishing the operating slip system. Both texture and dislocation analyses are consistent with the operation of these deformation systems. Recrystallization takes place extremely quickly at high temperatures (above 800 $^\circ\text{C}$), that is within seconds after deformation, and also dynamically during deformation itself. Recrystallization changes the texture such that $\langle 100 \rangle$ textures superimpose on the deformation texture. The flow stress peak observed during forging is found at a very high temperature. Possible origins of the peak are examined in terms of the operating slip systems.

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Microstructural characterization and solidification behavior of atomized Al-Fe powders

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The effect of solidification history on the resultant microstructure in atomized Al-2.56 wt% Fe and Al-6.0 wt% Fe powders was studied, with particular emphasis on droplet size, undercooling, and phase stability. The atomized Al-Fe powders exhibited four microstructural features, i.e. Al_3Fe phase (now known as $\text{Al}_{13}\text{Fe}_4$), Al + Al_3Fe , α -Al dendrite, and a pre-dendritic microstructure. The presence of these phases was noted to depend on alloy composition and a kinetic phase competitive growth mechanism due to the initial undercooling experienced by the powders. The occurrence of structures of

the predendritic, cellular, and/or dendritic type was properly predicted by the theory of dendrite growth into undercooled alloy melts for the case of large undercoolings.

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Corrosion of martensitic and austenitic steels in liquid gallium

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The compatibility of 1.4914 martensitic steel and 316 L austenitic stainless steel has been studied in the presence of static liquid gallium. It was shown that the materials are severely attacked by the liquid metal. The corrosion is characterized by the formation of a reaction layer identified as FeGa_3 . Depending on the steel, the growth kinetics and the morphology of the layer are found to be different. In the case of 1.4914 steel, the growth law is linear, which implies an interface controlled regime. Moreover, the layer formed from an initially rectangular substrate exhibits a typical cruciform pattern. In the case of 316 L steel, a parabolic growth is found after a transient period, indicating a process mainly controlled by diffusion. Contrary to the martensitic steel, the morphology of the layer occurring during the solid-liquid interaction leads to complete coverage of the 316 L substrate with rounded edges.

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In situ scanning electron microscopy study of eutectic SnPb and pure Sn wetting on Au/Cu/Cr multilayered thin films

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Wetting behavior of eutectic SnPb and pure Sn on Au(500 Å)/Cu(1 μm)/Cr(800 Å) layered thin films were monitored *in situ* in a ramping temperature profile using a scanning electron microscope (SEM) with a vacuum of 10^{-5} – 10^{-6} Torr. We found that the wetting behavior of these two solders in SEM were dramatically different from their behavior in RMA soldering flux; a smaller wetting angle and rough wetting front morphology were observed. Very surprisingly, no dewetting could be observed inside the SEM chamber, yet dewetting happened to the same sample when it was removed from the SEM and immersed in RMA soldering flux. We estimate the interfacial energy between liquid Sn and solid Cr and assume the reduction of surface and interfacial energies caused by possible oxidation of Cr and liquid Sn surface in the SEM in order to explain the above-mentioned wetting and dewetting behaviors.

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Phase transformations in ball-milled iron-rich Sm-Fe(-C) powders

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(McGill University)

Two intermetallic phases, R_2Fe_{17} carbide and $\text{R}_2\text{Fe}_{14}\text{C}$, which are promising candidates for permanent magnets, are formed in the iron-rich R-Fe-C ternary alloy system (R = rare earths). Using x-ray diffraction and thermomagnetometry the phase formation, transformation, and thermodynamic relations between the two structures, prepared by high energy ball milling, are studied quantitatively for R = Sm. The results lead to a free energy diagram for the pseudobinary system of $\text{Sm}_2\text{Fe}_{17}$ and C. A maximum equilibrium carbon content, x_c , has been established for the carbide $\text{Sm}_2\text{Fe}_{17}\text{C}_x$ and its temperature dependence determined. Beyond the equilibrium concentration, $\text{Sm}_2\text{Fe}_{17}\text{C}_x$ transforms into a mixture of $\text{Sm}_2\text{Fe}_{17}\text{C}_{x_c}$, $\text{Sm}_2\text{Fe}_{14}\text{C}$, and $\alpha\text{-Fe}$. Although not thermodynamically stable, $\text{Sm}_2\text{Fe}_{17}\text{C}_x$ can still be formed through nonequilibrium processes by being kinetically favored over the stable phase(s). This feature is important for the production of Sm-Fe-C-based permanent magnets.

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Soft x-ray absorption spectroscopy study of electrochemically formed passive layers on AISI 304 and 316L stainless steels

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The structure and composition of passive films electrochemically formed on AISI 304 and 316L stainless steels in a chloride-containing solution have been studied by soft x-ray absorption spectroscopy. Soft x-ray absorption spectra were taken at the oxygen *1s* edge and at the transition metals (Cr, Fe, Ni) *2p* edges, making it possible to determine the main contributions to the passive film's composition. The soft x-ray absorption spectra at the Cr *2p*

edges indicate that in all cases the passive film is mainly formed by Cr_2O_3 . Spectra at the Fe and Ni *2p* edges exhibit no significant contribution of Ni and Fe oxides to the passive layer composition. However, differences in spectral shape with respect to metallic Ni and Fe suggest the presence of a small amount of hydroxides, which is maximum for the AISI 304 stainless steel polarized at the lowest scan rate. The spectra at the O *1s* edges confirm the results obtained at the transition metal edges.

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The kinetics of indium/amorphous-selenium multilayer thin film reactions

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The reaction kinetics in vapor-deposited indium/amorphous-selenium (a-Se) multilayer thin films were studied using differential scanning calorimetry (DSC), x-ray diffraction (XRD), and transmission electron microscopy (TEM). A number of reactions were observed upon heating with characteristic temperatures which were found to be independent of the multilayer modulation wavelength. The initial interface reaction between In and a-Se is the formation of an In_2Se phase. Kinetic analyses of the In_2Se formation process combined with TEM observations indicated that interface reaction is characterized by the two-dimensional growth of pre-existing In_2Se regions formed during deposition to impingement in the plane of the original In/a-Se interface. The change of the density of In_2Se grains with temperature was analyzed in terms of the derived kinetic parameters; that is consistent with TEM observations and the heat release measurements.

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Phase transformation and thermal expansion of Cu/ZrW₂O₈ metal matrix composites

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Powder metallurgy was used to fabricate fully-dense, unreacted composites consisting of a copper matrix containing 50–60 vol% ZrW_2O_8 particles with negative thermal expansion. Upon cycling between 25 and 300 °C, the composites showed coefficients of thermal expansion varying rapidly with temperature and significantly larger than predicted from theory. The anomalously large expansion on heating and contraction on cooling are attributed to the volume change associated with the allotropic transformation of ZrW_2O_8 between its high-pressure γ -phase and its low-pressure α - or β -phases. Based on calorimetry and diffraction experiments and on simple stress estimations, this allotropic transformation is shown to result from the hydrostatic thermal stresses in the particles due to the thermal expansion mismatch between matrix and reinforcement.

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Strain sensing using carbon fiber

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Carbon fiber provides strain sensing through change in electrical resistance upon strain. Due to piezoresistivity of various origins, a single carbon fiber in epoxy, an epoxy-matrix composite with short carbon fibers (5.5 vol%), a cement-matrix composite with short carbon fibers (0.2–0.5 vol%), and an epoxy-matrix composite with continuous carbon fibers (58 vol%) are strain sensors with fractional change in resistance per unit strain up to 625. A single bare carbon fiber is not piezoresistive, but just resistive.

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Low volume fraction SiC_p/AA 380.0 composites fabricated by vacuum infiltration

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A vacuum infiltration process has been developed to fabricate the aluminum matrix composites reinforced with low volume fraction (< 50 vol%) of SiC_p . Generally, it is difficult to fabricate low volume fraction particulate composites by traditional infiltration processes because the particles always pack up to about 50 vol% in the preforms or compacts. In this study, the powder compacts were prepared of the well-mixed Ni-coated SiC_p and pure aluminum powders and then were packed in quartz tubes. An aluminum alloy (Al-8.7% Si-2.6% Cu) with a composition similar to AA 380.0 was used to

infiltrate these compacts. Experimental results showed that the infiltration temperature of 640 °C is favorable for the fabrication of these composites. Infiltration behavior, microstructure, nickel distribution, bending test, and fractography of the composites were investigated.

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Interfacial characterization using transmission electron microscopy examination of the diffusion bonding of SiC whisker-reinforced aluminum alloys

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This paper describes the microstructural characterization, using transmission electron microscopy (TEM), of the solid-state, diffusion-bonded interfaces generated in a SiC whisker-reinforced aluminum composite. Diffusion bonding was carried out using an aluminum-lithium alloy as the bonding interlayer. Two kinds of bonded interface were studied: those generated between the composite matrix and the metallic interlayer (metallic-metallic) and other ceramic-metallic interfaces formed between the interlayer and the SiC whiskers. The first showed the formation of zones of recrystallization across the original bond interface, and the second generally presented a high degree of continuity without the formation of interface reaction layers between the SiC whiskers and the interlayer. However, the formation of a degradation oxide layer was detected in some of the whisker/interlayer diffusion bonds. Its presence is due to the reaction between the alloying elements of the Al-Li interlayer and the SiO₂ layer which surround some of the whiskers of the parent composite.

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The interfacial reaction in Cr₃C₂/Al₂O₃ composites

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This study investigates the effects of sintering atmosphere and temperature on the interfacial properties of Cr₃C₂/Al₂O₃ composite. Thermodynamic considerations and calculations with computer-assisted methods for the equilibrium compositions in the Al-O-Cr-C system were used to simulate the interfacial reaction in Cr₃C₂/Al₂O₃ composite during sintering. The results were in good agreement with the experimental analysis. Cr₃C₂ is more stable during sintering in a system with carbon due to the lower equilibrium oxygen partial pressure. Controlling CO and O₂ gas concentration, Cr₃C₂ firstly oxidized, decarbonized, and then transformed to Cr₇C₃ before reacting with Al₂O₃. An interfacial reaction between Cr₃C₂ and Al₂O₃ was not observed.

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Synthesis, structural, and morphological characterization of ceramics in the system Bi₂O₃-TiO₂-CuO

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This paper reports the formation of a solid solution in the system Bi₂O₃-TiO₂-CuO. This solid solution seems to be isostructural with Bi₄Ti₃O₁₂, according with the x-ray powder diffraction patterns. Microstructural studies done using scanning electron microscopy show the typical elongated Bi₄Ti₃O₁₂ grain morphology only in samples with 2 : 2 : y molar ratios of the Bi₂O₃ : TiO₂ : CuO oxides (y = 1, 2, or 3).

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Microstructural studies of boron nitride films deposited by microwave plasma-assisted chemical vapor deposition by using trimethyl borazine precursor

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This film of cubic boron nitride (c-BN) were synthesized using an organometallic precursor trimethylborazine (TMB) which contains both boron and nitrogen in 1 : 1 stoichiometric ratio. The films were deposited at different temperatures ranging from 300 to 500 °C at a pressure of 2 Torr and at 360 W microwave power, using N₂ as carrier gas. The deposited films were characterized by Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), and scanning electron microscopy (SEM) which reveal the presence of amorphous BN and crystalline c-BN in varying proportions. The x-ray dif-

fraction pattern of the deposited films showed a strongest peak at 2θ = 57.1° where the interplanar distance value δ = 2.06 Å agreed well with the (111) crystallographic orientation of c-BN phase.

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Preparation of a ZrO₂-Al₂O₃ nanocomposite by high-pressure sintering of spray-pyrolyzed powders

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ZrO₂-Al₂O₃ powders were synthesized by spray pyrolysis. These powders were sintered at 1 GPa in the temperature range of 700–1100 °C. The microstructural evolution and densification are reported in this paper. The application of 1 GPa pressure lowers the crystallization temperature from ~850 to <700 °C. Similarly, the transformation temperature under 1 GPa pressure for γ → α Al₂O₃ reduces from ~1100 to 700–800 °C range, and that for t → m ZrO₂ reduces from ~1050 to 700–800 °C range. It was possible to obtain highly-dense nanocrystalline ZrO₂-Al₂O₃ composite at temperatures as low as 700 °C. The effect of high pressure on nucleation and transformation of phases is discussed.

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The structural transformation of anatase TiO₂ by high-energy vibrational ball milling

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The structural transformation of anatase TiO₂ by high-energy vibrational ball milling was studied in detail by different analytical methods of x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). This structural transformation involves both phase transition and nanoparticle formation, and no amorphization was observed. The crystallite size was found to decrease with milling time down to nanometer-size ~13 nm and approaching saturation, accompanied by phase transformation to metastable phases, i.e. TiO₂ (II), which is a high-pressure phase and TiO₂ (B), which was identified in ball-milled powder reported for the first time in this paper. These phases eventually started transforming to rutile by further milling.

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Restructuring of alumina particles using a plasma torch

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A method to modify ceramics using a low power microwave plasma torch is described. To wit: The size, shape, surface area, and phase of alumina particles were dramatically modified by passage through an atmospheric pressure argon plasma, operated at 1 kW or less power. Specifically, irregularly shaped particles of γ-alumina with an average diameter of 11 μm were converted to smaller (ca. 4 μm) spherical particles primarily consisting of δ- and α-(corundum) phases. Also notable was the finding that modifications of the particles, such as changes in surface area, correlate to applied plasma energy. The plasma torch was operated with an argon flow rate of 5 slpm, power of between 400 and 1000 watts, and average particle residence time in the plasma of 0.1 s.

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Crystal growth of layered perovskite Sr₂Nb₂O₇ and Sr₂Ta₂O₇ film by sol-gel technique

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High dielectric and low loss capacitor thin films of Sr₂Nb₂O₇ (SN), Sr₂Ta₂O₇ (ST), and their solid solution Sr₂(Nb_xTa_{1-x})₂O₇ (SNT) were investigated using the sol-gel technique. The SN film grows with the (0n0) orientation in the case of heating at over 700 °C. Heat treatment at a lower temperature results in the polycrystal ST-type structure. The SNT at x < 50% also resulted in the ST-type. The dielectric constant for the SN film was 45, within 10% variation at ±0.5 MV/cm. Dielectric loss (tan δ) was 0.3–0.5%. The small variation in dielectric constant and the paraelectricity with low loss are suitable for capacitor applications.

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Grain boundary impedance of doped Mn–Zn ferritesD. Arcos,* M. Vázquez,* R. Valenzuela,* M. Vallet-Regí#
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The electrical properties of Mn–Zn ferrites undoped and doped with Nb₂O₅ and V₂O₅ were investigated by impedance spectroscopy. The observed impedance response corresponded to that of a highly resistive grain boundary component in series with a less resistive bulk component. The presence of Nb⁵⁺ and V⁵⁺ led to an enhancement in the electrical resistance, especially in grain boundaries, as well as a greater difference in the electrical behavior between bulk and grain boundary components. The different dopant performance of these two components is discussed on the basis of grain boundary structure and chemical data, electrical conductivity, and dielectric dispersion.

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Relation between coarsening and densification in solid state sintering of ceramics: Experimental test on superfine zirconia powder compacts

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Coarsening (including grain growth and pore growth) and densification behavior of superfine Y-TZP and YSZ powder compacts in the intermediate stage were investigated. It has been found that grain growth in the compacts is basically not affected by the compaction properties, and pore growth is driven by both grain growth and densification. Grain growth alone leads to size-proportional pore growth, and densification results in pore shrinkage. The relation between grain size and density is analyzed to be linear when grain growth and densification are believed to be driven by different stresses under an identical diffusion process. Both theoretical and experimental results show that compaction properties and the heating rate do not alter this linear relation between grain size and density but influence the slope of the linear relation. Larger dihedral angle, higher grain density, and narrower particle and pore size distributions are found favorable for the achievement of the grain size density trajectory with promoted densification and minimized grain growth.

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Particle-shape control and formation mechanisms of hydrothermally derived lead titanateJ. Moon, M.L. Carasso, H.G. Krarup, J.A. Kerchner, J.H. Adair
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Phase-pure perovskite lead titanate with various morphologies has been synthesized by a hydrothermal method at 150 °C. Particle shapes include cubic, tabular, and aggregated spherical platelike shapes. The feedstock concentration greatly influences particle morphology of the hydrothermally derived PbTiO₃. At a concentration of 0.05 M, the tabular particles form while cubic particles are produced at 0.1 M. Aggregated spherical platelike particles are synthesized at 0.125 M. It was observed that both tabular and cubic particles directly precipitate from the coprecipitated precursor gel. In contrast, the platelike-shaped intermediate phase appears during the initial stage of reaction at 0.125 M and *in situ* transforms into perovskite PbTiO₃ during further hydrothermal treatment. The intermediate phase preserves its particle shape during transformation and, acting as a template, gives rise to the final tabular PbTiO₃ particles. It is demonstrated that only base reagents such as KOH and NaOH, which provide a highly basic condition (i.e. pH > 14), promote transformation of the coprecipitated gel into the perovskite PbTiO₃. A Hancock and Sharp kinetic analysis in conjunction with microstructural evidence suggests that the formation mechanism is dissolution and recrystallization in which the degree of supersaturation plays an important role in dictating the crystallographic particle phase and morphology of the particles. An experimentally constructed solubility diagram indicates that an excess lead condition is necessary to compensate for loss of lead species and to increase supersaturation to expedite precipitation of PbTiO₃ at highly alkaline conditions.

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Combustion synthesis of α-Si₃N₄ whiskers

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α-Si₃N₄ whiskers were fabricated firstly through combustion synthesis (CS) technology. The as-synthesized crystals with [001] as the elongated axis contain a large amount of linear defects including (a+b)-type, (a+b+c)-type, and c-type of dislocations. The growth of α-Si₃N₄ whiskers is mainly con-

trolled by vapor-condensation (VC) mechanism. Special additive plays an important role in promoting the growth of α-Si₃N₄ whiskers and suppressing the phase transformation of α-Si₃N₄ to β-Si₃N₄.

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Microstructure and ambient properties of a Sialon composite prepared by hot pressing and reactive sintering of β-Si₃N₄ coated with Al₂O₃G. Ghosh,* S. Vaynman,* M.E. Fine,* S.M. Hsu+
(*Northwestern University, +NIST)

A composite microstructure, consisting of β Sialon, O-Sialon, and X-Sialon phases, has been produced by coating β-Si₃N₄ particles with amorphous alumina followed by hot pressing and reactive sintering at 1923 K. The particle coating procedure was selected over conventional powder blending in order to promote heterogeneous nucleation of β-Sialon grains on β-Si₃N₄ particles uniformly. The microstructure, chemistry of the phases, and interphase interfaces of this ceramic were characterized by transmission electron microscopy (TEM) and high resolution analytical electron microscopy (AEM). Both electron energy-loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) x-ray microanalysis in AEM revealed that β-Sialon grains had varying aluminum and oxygen contents. High-resolution electron microscopy (HREM) examination of several interphase interfaces and triple junctions suggests that the amount of glassy phase in the produced ceramic is substantially lower compared to those reported in the literature. This is of importance of high temperature properties. The fracture toughness and wear properties were evaluated at room temperature. Available data indicate that the fracture toughness and wear of β-Sialon composite can be significantly improved by the powder coating technique compared to the conventional powder blending technique.

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Effects of PbO excess in Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ ceramics: Part I. Sintering and dielectric propertiesM. Villegas,* A.C. Caballero,* M. Kosec,* C. Moure*, P. Duran,*
J.F. Fernandez*
(*CSIC, *Jozef Stefan Institute)

The influence of the presence of free PbO on densification, the perovskite/pyrochlore phase ratio, and corresponding dielectric properties has been studied for 0.9 PMN–0.1 PT-based ceramics with different added PbO excess. The sintering behavior of PMN–PT-based ceramics was basically controlled by PbO losses. However, the presence of a rich-PbO liquid phase during sintering produced pyrochlore grains, mainly located at the surface of the specimens. The dielectric properties of the PMN–PT-based materials, fabricated with different values of PbO excess, were similar when the secondary phase preferentially located at the surface was removed by polishing prior to electrode deposition. The thickness of the PbO-rich intergranular layers of the four samples with different initial PbO content was mainly independent of the amount of PbO excess because most of the free PbO was eliminated during sintering. Dielectric constant values of approximately 17000 at 1 kHz and 40 °C were measured.

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Effects of PbO excess in Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ ceramics: Part II. Microstructure developmentM. Villegas,* J.F. Fernández,* A.C. Caballero,* Z. Samardija,+ G. Drazic,+
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(*CSIC, *Jozef Stefan Institute)

The microstructure evolution of Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ (PMN–PT) based ceramics has been investigated to determine the influence of the presence of PbO content in excess of stoichiometric values. The microstructure of the different materials showed a different evolution of secondary phases (free PbO and pyrochlore type) related to the PbO excess. The pyrochlore phase appeared in a layer near the top surface of the specimens. The thickness of the layer and the grain size of this secondary phase increased with the amount of PbO excess. A transmission electron microscopy (TEM) study of the sintered specimens revealed a core-shell structure in more than 30% of grains. The shell of these grains was Ti-rich PMN, and it is related to the presence of a liquid-phase-assisted sintering mechanism.

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Synthesis and sintering of SiC under high pressure and high temperature

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(National Aerospace Laboratories)

Starting from elemental powders, simultaneous synthesis and compaction of SiC were conducted at 3 GPa pressure and temperatures in the range 2100–2900 K. The sintered compacts were characterized by x-ray diffraction, microhardness measurements, and microscopic studies. The efficiency of formation of SiC was dependent on the particle size of the silicon powder, crystallinity of the reactant carbon, molar ratio of silicon and carbon, and synthesis temperature and time. Carbon in excess of the stoichiometric amount was required to obtain compacts free from residual silicon. The SiC samples, with Si : C molar ratio 1 : 1.05, prepared at 2100 K for 300 s had a density and hardness of 3.21 g/cm³ (98.8% of theoretical density) and 22 Gpa, respectively. The crystal structure of the SiC depended on the synthesis temperature. Pure β -SiC in the temperature range 2100–2500 K, and a mixture of α - and β -SiC above 2500 K were obtained. The β -SiC was highly crystalline and nearly defect-free.

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Bulk thermal expansion for tungstate and molybdates of the type A₂M₃O₁₂

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(Oregon State University)

Bulk thermal expansion properties of 19 members of the A₂M₃O₁₂ family of tungstates and molybdates were determined from room temperature to 800 °C. The observed behavior ranges from strong negative thermal expansion ($\alpha = -11 \times 10^{-6} \text{ K}^{-1}$) in Sc₂W₃O₁₂ to near zero thermal expansion in

Al_{1.68}Sc_{0.02}In_{0.30}W₃O₁₂

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Reaction synthesis of mullite-zirconia from mixtures of alumina, silica, and 3 mol% yttria-zirconia powders

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(Tatung Institute of Technology)

Mullite-zirconia composites were synthesized by reaction-sintering powder mixtures of α -alumina, amorphous silica, and 3 mol% yttria-stabilized zirconia. It is found that the addition of 3 mol% yttria-zirconia improves sintering and lowers the mullitization temperature. It also suppresses the cristobalite formation and enhances zircon formation between 1300 and 1400 °C. Results further suggest that these effects are consequences of modification of the silicate glass by yttria. Samples containing ≥ 20 vol% of 3 mol% yttria-zirconia could be sintered at 1500 °C for 2 h to obtain dense composites consisting of mullite and tetragonal zirconia. The microstructural investigations of the sintered samples support the viewpoint that mullite formation is via nucleation and growth from aluminosilicate glass. They also reveal that zirconia can hinder the grain growth of mullite and that the coalescence of zirconia grains is accomplished by grain boundary diffusion.

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Field-activated pressure-assisted combustion synthesis of polycrystalline Ti₃SiC₂

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(University of California)

The simultaneous synthesis and densification of the ternary Ti₃SiC₂ was investigated by the field-activated, pressure-assisted combustion method. Depending on temperature and time at temperature, relatively pure and nearly fully dense materials can be synthesized by this approach. The optimum conditions to produce this phase were a reaction temperature of 1525 °C and a time at temperature of 2 h. The product contained TiC as a second phase at a level of ≤ 2 mol%. The resulting ternary phase has the typically elongated grains which were about 25 μm in size. Within a range of applied force of 1–4 N, the microhardness of the product was relatively constant, ranging from 6 to 7 GPa. Investigations on the thermal and chemical stabilities of the ternary were also conducted. Vacuum annealing at temperatures of 1600 and 2000 °C resulted in the formation of a surface layer of TiC, while the air-annealing at 1000 °C resulted in the formation of TiO₂. Oxidation studies on the prepared Ti₃SiC₂ were made at temperatures ranging from 800 to 1100 °C. The results suggest a two-mechanism process, one dominating in the approximate range of 800–950 °C and the other in the range 950–1100 °C with corresponding activation energies of 137.7 and 312.5 kJ. mol⁻¹. The results are

explained in terms of two proposed reactions on the basis of microprobe analyses.

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Pulsed laser-ablation deposition of thin films of molybdenum silicide and its properties as a conducting barrier for ferroelectric random-access memory technology

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We report on the feasibility of using molybdenum silicide as a conducting barrier for integration of ferroelectric lead zirconate titanate capacitors on Si. Thin films of MoSi₂ were deposited by pulsed laser-ablation deposition (PLD). The silicide films showed a structural transition from amorphous to orthorhombic to tetragonal phase as the temperature of deposition was changed from room temperature to 900 °C. The four-probe resistivity and surface roughness of the films decreased with an increase in the deposition temperature and crystallinity of the phase. Ferroelectric (La,Sr)CoO₃/Pb(Nb,Zr,Ti)O₃/(La,Sr)CoO₃ capacitors were grown on Si/poly Si/MoSi₂ and Si/poly Si/Pt/MoSi₂ structures. Transmission electron microscopy (TEM) studies of the MoSi₂/LSCO and MoSi₂/Pt/LSCO heterostructures indicated the formation of a thin layer of SiO₂. In the case of Pt/MoSi₂, Pt reacts with the silicide and forms PtSi consuming the entire platinum layer and thus makes it unsuitable as a composite barrier. Electrical testing of the LSCO/PNZT/LSCO capacitors through capacitive coupling showed desirable ferroelectric properties on these substrates.

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The influence of the external stress on the electromechanical response of electrostrictive 0.9Pb(Mg_{1/3}Nb_{2/3})O₃-0.1PbTiO₃ in the dc electrical field biased state

J. Zhao, V. Mueller, Q.M. Zhang
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The influence of uniaxial compressive stress, T₃, applied parallel to the electrical field, on the electromechanical parameters of 0.9Pb(Mg_{1/3}Nb_{2/3})O₃-0.1PbTiO₃ ceramics in the dc electrical field biased state and at temperatures near the dielectric constant maximum T_m was investigated. It was found that T₃ reduces both the dielectric constant and polarization level which results in a reduction of the piezoelectric coefficient with stress. However, the compliance of the material does not show much change with stress. As a consequence, the coupling factor k₃₃ is also reduced with stress. On the other hand, the existence of the local micropolar region in the material causes anomalous changes in the aforementioned properties when the material is subjected to a high electric field, which induced a macropolar state. The transformation of this macropolar state back to a micropolar state under stress involves a large volume strain and results in an enhancement of the hydrostatic piezoelectric response.

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Synthesis and sintering of rare-earth-doped ceria powder by oxalate coprecipitation method

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(Kagoshima University)

Doped ceria, which has a higher oxygen ion conductivity than yttria-stabilized zirconia, is one of the possible electrolytes for solid oxide fuel cell at low temperatures. This study concerns powder preparation and densification of rare-earth-doped ceria. Rare-earth-doped ceria powders with a composition of Ce_{0.8}R_{0.2}O_{1.9} (R = Yb, Y, Gd, Sm, Nd, and La) were prepared by heating the oxalate coprecipitate when a mixed rare-earth/cerium nitrate solution was added to an oxalic solution. The oxalate and derived-oxide powders were characterized by x-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG-DTA), particle size analyzer with laser diffraction, inductively coupled plasma (ICP), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). This method provided the oxalate solid solutions containing Ce and R, which were calcined to form the oxide solid solutions at 600 °C in air. The lattice parameter of oxide powders increased linearly with increasing ionic radius of doped rare earth. The size of platelike particles of oxalates and oxides depended on the concentration of oxalic acid and showed a minimum at 0.4 M oxalic acid. Dry milling of oxide N powder with α -Al₂O₃ ball was effective to reduce the sizes and aspect ratios of particles with little contamination of Al₂O₃. These rare-earth-doped ceria powders with

various sizes were formed by uniaxial pressing (49 MPa) followed by cold isostatic pressing (294 MPa), and sintered at 900–1600 °C in air for 4 h. The micrometer-sized doped CeO₂ powders were densified above 95% of the theoretical density at 1200 °C. The grain sizes of rare-earth-doped ceria after sintering at 1600 °C were larger in the samples with the larger rare earth element.
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Formation and self-organization of nanometer-scale Au particles on graphite by vacuum deposition in iodine vapor

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Vacuum depositions of Au on highly oriented pyrolytic graphite (HOPG) and SiO₂ substrates in iodine vapor of 1×10^{-4} Torr give rise to formation of dispersed nanoscale Au particles at room temperature. The iodine is physisorbed on the Au surface and prevents the Au particles from coalescing. The mean diameter of Au particles on HOPG is about 40 nm, which is larger than that on SiO₂. The particles on HOPG have a narrower and more uniform size distribution than those on SiO₂. Radial distribution function of the particles on HOPG showed many well-defined peaks, whereas that on SiO₂ had only one peak, indicating highly structured deposition on HOPG by iodine adsorption.

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Comparison of (hexafluoroacetylacetonate)Cu(vinyltrimethylsilane) and (hexafluoroacetylacetonate)Cu(allyltrimethylsilane) for metalorganic chemical vapor deposition of copper

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For the metalorganic chemical vapor deposition (MOCVD) of copper, (hfac)Cu(VTMS) (hfac = hexafluoroacetylacetonate, VTMS = vinyltrimethylsilane) and (hfac)Cu(ATMS) (ATMS = allyltrimethylsilane) were compared, and the effect of L ligand in (hfac)Cu-L was examined. It was found out by ¹H-NMR (nuclear magnetic resonance) that thermal stability of (hfac)Cu(VTMS) was better than that of (hfac)Cu(ATMS) due to the relatively weak Cu-ATMS bond. From *in situ* Fourier transform infrared spectroscopy (FTIR) experiments, the formation of Cu(hfac)₂, the product of disproportion reaction of Cu(hfac) was observed in the gas phase, and (hfac)Cu(ATMS) was found to be more reactive to form Cu(hfac)₂. The minimum temperature for the deposition of copper films from (hfac)Cu(ATMS) was as low as 60 °C, which was about 70 °C lower than from (hfac)Cu(VTMS). The grain size of the film deposited with (hfac)Cu(ATMS) was substantially larger than that with (hfac)Cu(VTMS), which showed that the chemical reactivity of the precursor had an influence on the microstructure along with the deposition temperature.

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Absolute total energy of small copper clusters in an all-electron mixed-basis approach with the generalized-gradient approximation

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#National Industrial Institute of Nagoya)

In order to investigate the absolute value for the total and exchange-correlation energies of small transition metal clusters, an all-electron mixed-basis approach with the generalized gradient approximation (Perdew-Wang's GGA-1) is applied for the first time to small Cu clusters. We find that the GGA significantly deepens (2.57–2.59 a.u. per atom) both the total and exchange-correlation energies obtained with the local density approximation. A better agreement is obtained with experiments for the binding energy of Cu₂ when the spin-dependent calculation is used for an isolated Cu atom.

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Interdiffusion in Ni₈₀Fe₂₀/Mo magnetic multilayers prepared by magnetron sputtering

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The interdiffusion in Ni₈₀Fe₂₀/Mo magnetic multilayers with a repeat length of 3.4 nm has been investigated using x-ray diffraction (XRD) technology. The multilayers have been fabricated by using a magnetron sputtering system. The decay with annealing time in the intensity of the first-order x-ray

satellite peak arising from the composition modulation was used to determine the effective interdiffusion coefficient D_{λ} . As the annealing temperature is below 483 K, the interdiffusion is found to be relatively slow ($D_{\lambda} < 8.88 \times 10^{-25}$ m²/s). This result suggests that the Ni₈₀Fe₂₀/Mo multilayers have a strong resistance to the atomic interdiffusion between sublayers. The diffusivities over the temperature range 343–683 K have an Arrhenius-type temperature dependence with a pre-exponential factor $D_0 = (4.02 \pm 1.21) \times 10^{-22}$ m²/s and an activation enthalpy of about 0.26 ± 0.08 eV. The much lower activation enthalpy is attributed to the coherence strains existing in the multilayers.

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Ultraviolet laser-induced formation of thin silicon oxide film from the precursor β -chloroethyl silsesquioxane

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(University of Pennsylvania)

Formation of silicon oxide thin films from spin-coated β -chloroethyl silsesquioxane (β -cesq) on silicon, NaCl, and Quartz was induced by 193 nm laser pulses. The silicon oxide deposition is characterized by ir, uv, ellipsometry, and Rutherford backscattering spectrometry. The silicon oxide films obtained by uv irradiation were found to have much less carbon and chlorine as impurities and have a higher refractive index as compared to those obtained by annealing. The photoinduced oxide films were found to be smooth, without laser-induced micro-rough or periodic structures.

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Composition, oxidation, and optical properties of fluorinated silicon nitride film by inductively-coupled plasma-enhanced chemical vapor deposition

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Amorphous fluorinated silicon nitride films have been deposited with the variation of NF₃ flow rate using SiH₄, N₂, Ar, and NF₃ gases by inductively-coupled plasma-enhanced chemical vapor deposition for the first time, and the absolute composition, oxidation mechanism, and optical properties were investigated. The absolute composition including hydrogen was performed by means of elastic recoil detection time of flight. It was found that the oxygen and fluorine contents in the film dramatically increased, but the hydrogen content decreased to below 4 at.% as the NF₃ flow rate increased. The oxidation mechanism could be explained in terms of the incorporation of the activated residual oxygen species in the chamber into the film with unstable open structure by the fluorine-added plasma. It was shown that the density and optical properties such as refractive index, absorption coefficient, and optical energy gap depended on the film composition. The variations of the above properties for fluorinated silicon nitride film could be interpreted by the contents of fluorine and oxygen with high electronegativity.

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Thermodynamic analysis of solid-state metal/Si interfacial reactions

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An attempt has been made to interpret the experimentally reported transitions of layer sequences during the Co/Si, Ti/Si, and Ni/Si interfacial reactions in a consistent way and to build a thermodynamic calculation scheme that enables it. The basic ideas are that the silicide with the highest driving force of formation under a metastable local equilibrium state at an interface would form first at the lowest temperature and that when several silicides can nucleate simultaneously and compete for growth at an initial stage of a high-temperature reaction, the one whose composition is closest to those of surrounding phases would form a continuous interfacial layer first and grow thicker. A critical review of literature information has also been made in order to clarify the first-forming silicide and silicide formation sequence in each metal/Si interfacial reaction. The observed first-forming crystalline silicides, CoSi, Ti₅Si₃, and Ni₂Si in each metal/Si interfacial reaction were in agreement with the present prediction based on the first idea. The reason why Co₂Si and C49 TiSi₂ have frequently been observed in high temperature Co/Si and Ti/Si reactions as if they were the first-forming crystalline silicides could also be explained based on the second idea. By combining both ideas, a general thermodynamic calculation scheme that can be applied for analysis, rationaliza-

tion, and even prediction of interfacial reactions between different materials could be suggested.

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The effect of RuO₂/Pt hybrid bottom electrode structure on the leakage and fatigue properties of chemical solution derived Pb(Zr_xTi_{1-x})O₃ thin films

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We have investigated the effect of RuO₂ (10, 30, 50 nm)/Pt layered hybrid bottom electrode structure and film composition on the leakage and fatigue properties of chemical solution derived Pb(Zr_xTi_{1-x})O₃ (PZT) thin films. It was observed that the use of high Ti content (Zr : Ti = 30 : 70) films with control of excess PbO at the thin RuO₂ (10 nm)/Pt bottom electrode surface reduced leakage current and showed good fatigue properties with high remanent polarization compared to the use of high Zr films (Zr : Ti = 50 : 50) or thicker RuO₂ (30, 50 nm)/Pt bottom electrodes. Typical P-E hysteresis behavior of PZT films was observed even at an applied voltage of 3 V, demonstrating greatly improved remanence and coercivity. Fatigue and breakdown characteristics of these modified PZT thin films (Zr : Ti = 30 : 70) on RuO₂ (10 nm)/Pt, measured at 5 V, showed stable behavior, and less than 15% fatigue degradation was observed up to 10¹⁰ cycles.

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The influence of crystallization route on the SrBi₂Nb₂O₉ thin films

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Polycrystalline SrBi₂Nb₂O₉-layered ferroelectric thin films were synthesized on Pt/Ti/SiO₂/Si substrate using the polymeric precursors solution. The dip-coated films were specular and crack-free and crystallized during firing at 700 °C. Single, double, and triple-layered films were obtained by several dips in the deposition solution, and the influence of crystallization between each dip was studied. Microstructure and morphological evaluation were followed by grazing incident x-ray diffraction (GIXRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Multilayered films obtained using the intermediate-crystallized layer route present a dense microstructure with spherical grains with a preferential orientation in <215> direction; films obtained using the intermediate-amorphous layer route are polycrystalline and present elongated grains around 250 nm in size.

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Microstructure, electrical properties, and thermal stability of Ti-based ohmic contacts to n-GaN

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Single Ti layers, single TiN layers, and thin Ti films overlaid with Au were investigated as ohmic contacts to n-type (n = 4.5 × 10¹⁷ to 7.4 × 10¹⁸ cm⁻³) single-crystal GaN (0001) films. Transmission line measurements (TLM) revealed the as-deposited TiN and Au/Ti contacts on n = 1.2 × 10¹⁸ cm⁻³ to be ohmic with room-temperature specific contact resistivities of 650 and 2.5 × 10⁻⁵ Ω · cm², respectively. Single Ti layer contacts had high resistance and were weakly rectifying in the as-deposited condition. The three contact/GaN systems exhibited a substantial decrease in resistivity after annealing; the value of ρ_c was also a function of the carrier concentration in the GaN. The Au/Ti contacts exhibited the lowest resistivity values yet observed in these contact studies, particularly for the more lightly doped n-GaN. The ρ_c for n = 1.2 × 10¹⁸ cm⁻³ reached 1.2 × 10⁻⁶ Ω · cm²; for n = 4.5 × 10¹⁷ cm⁻³, ρ_c = 7.5 × 10⁻⁵ Ω · cm² after annealing both samples through 900 °C. X-ray photoelectron spectroscopy (XPS) and high-resolution cross-sectional transmission electron microscopy (X-TEM) analysis revealed the formation of TiN at the interface of annealed Ti layers in contact with GaN, which is believed to be beneficial for ohmic contact performance on n-GaN.

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Surface textured zinc oxide films

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Both epitaxial and crystallographically fiber-textured ZnO films can exhibit a surface texturing ("cratered") morphology when grown by pulsed

laser deposition at temperatures in the range of 350–750 °C in a background pressure of oxygen. The surface texturing is a consequence of the nucleation of oriented c axis grains that grow geometrically and impinge laterally. It is concluded that the surface texturing is due to nonequilibrium growth, being the result of a competition between the arriving flux, diffusive flux along the surface, and, possibly, concurrent ionetching from the laser-ablated plasma plume. At higher temperatures, no surface texturing occurs, presumably because of concurrent grain growth and more rapid surface smoothing by diffusion.

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Reduction of intrinsic stresses in chemical vapor deposition diamond

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Intrinsic stresses in chemical vapor deposition (CVD) diamond were controlled by multistep processing. Film stresses (thermal and intrinsic) were measured with the bending plate method. The thermal stresses are compressive and arise due to the mismatch in thermal expansion coefficient between the film and substrate. The intrinsic stresses are tensile and evolve during the deposition process. These stresses increase with deposition time. An intermediate step consisting of annealing the film when the diamond crystallites are only partially coalesced reduces the intrinsic stress by more than 50%. Annealing at longer growth times (i.e. after complete coalescence) does not produce large reductions in intrinsic stress. Our results are consistent with stress generation due to the formation of nonequilibrium grain boundary structures. The intermediate annealing step does not produce a large, direct stress reduction; instead, it alters the film microstructure in some subtle way, which reduces stress generation during subsequent growth.

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Characterization and optical properties of diamondlike carbon prepared by electron cyclotron resonance plasma

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Diamondlike carbon (DLC) films have been prepared on radio-frequency (rf) biased substrates maintained at low temperature using electron cyclotron resonance (ECR) CH₄-Ar plasma. The effects of negative rf bias and reactant gas composition on the bonding structure, hardness, and resistivity of the films were systematically investigated. DLC films deposited on PMMA (polymethyl methacrylate) were examined by optical methods to determine the absorption coefficients and the optical band gap. It was found that DLC films synthesized at bias voltage of -(80–100) V and F_{CH₄}/F_{Ar} of 0.075–0.086 exhibit extreme hardness of more than 3000 kgf mm⁻², high electrical resistivity up to 10¹⁴ Ω · cm, band gap larger than 2.5 eV, and excellent optical transparency. The results indicate that ECR CH₄-Ar plasma with low negative rf bias and suitable CH₄/Ar gas ratio can process optically transparent and hard protective DLC films on PMMA plastics.

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Determination of shear viscosity of borosilicate glass + silica powder compacts by an optical system

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The shear viscosity of borosilicate glass (BSG) + silica powder compacts was determined during isothermal sintering at temperatures between 665 and 715 °C. An optical system was used to measure *in situ* the densification profiles of the compacts in the form of thick films constrained on a rigid substrate and in-plane stresses generated during sintering. The shear viscosity as a function of relative density was calculated from these measurements by using Scherer's viscous constitutive equations for a porous sintering body. The shear viscosity for samples with silica contents from 0 to 20 vol% generally showed a slow increase with density in the low-density regime followed by a rapid rise after some threshold density that decreased with either increasing silica powder content or decreasing sintering temperature. The dependence of shear viscosity on relative density is consistent with results from sinter-forging experiments. However, results obtained from pure BSG compacts also revealed strong dependence of shear viscosity on temperature and microstructure, which has been all but neglected in previous theoretical studies.

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Synthesis and characterization of nonconventional nickel-titania glasses by sol-gel routeT.K. Kundu,* D. Chakravorty*⁺(*Indian Association for the Cultivation of Science, ⁺Jawaharlal Nehru Centre for Advanced Scientific Research)

Glasses in the NiO–TiO₂ system in the composition range 15 to 25 mol% of NiO have been synthesized by sol-gel technique by heat treatment of the precursor sol at 500 °C. The glass structure is built up by crosslinking of two units, namely TiO₆ octahedron and NiO₃ triangle. Glassy structure is confirmed at a microscopic level by scanning electron microscopy. An increase in the values of peak-to-peak width of electron paramagnetic resonance with increasing concentration of Ni²⁺ is attributed to an enhanced interaction between neighboring paramagnetic Ni²⁺ ions.

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Nonlinear optical properties of TeO₂-based glasses: (Li and K)₂O–TeO₂ binary glasses

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The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of the $x\text{Li}(\text{Na and K})_2\text{O} \cdot (100 - x)\text{TeO}_2$ binary glasses have been measured by the third harmonic generation (THG) method. It is found that the $\chi^{(3)}$ of each series of glasses decrease with increasing alkali oxide content. The largest $\chi^{(3)}$ values obtained are about 1.3×10^{-12} esu for a 7.5Li₂O • 92.5TeO₂ glass, being about 45 times larger than that of fused silica glass for the present series samples. For the purpose of investigating the relationship between the $\chi^{(3)}$ and the optical parameters, such as linear refractive index, polarizability per unit volume which is represented by term $(n_o^2 - 1)/(n_o^2 + 2)$, dispersion energy (E_d) which is related to the Abbe number and excitation energy (E_0) which is closely related to the optical band gap (E_g), we derived the equations which relate the $\chi^{(3)}$ to optical parameters on the basis of Lines' model. Finally, it was experimentally confirmed that the $\chi^{(3)}$ value of alkali oxide-TeO₂ glasses is proportional to the term $(n_o^2 + 2)^3(n_o^2 - 1) \cdot E_d/E_0^2$.

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Atomic force microscopy study of small-size nanotubular polymer thin films

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In this paper, we report atomic force microscopy (AFM) images of a tubular polymer and its supermolecular polymer thin films, operated in contact mode at room temperature in air. The configuration models are also calculated using molecular dynamics. The diameter of the polymer nanotube is about 0.7 nm, the smallest size a tube can have. The results of calculations agree with the experimental results.

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Optical properties of heat-treated polyparaphenylene

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The optical properties of heat-treated polyparaphenylene (PPP) were investigated by means of Raman and photoluminescence (PL) spectroscopy. Special attention is given to PPP heat-treated to temperatures (T_{HT}) near the carbonizing temperature region ($T_{HT} \approx 700$ °C), since polymer-based carbonaceous compounds with low- T_{HT} (<1000 °C) have been found to exhibit electrochemical properties that strongly contrast both the as-prepared polymer and fully carbonized samples. The Raman spectra show that for T_{HT} in the range 650–725 °C, several Raman bands near 1300 cm⁻¹ can be correlated with both ground-state benzenoid and excited-state quinoid PPP A_g modes. An increase in quinoid character is observed with increasing T_{HT} , which is consistent with the theoretically predicted stabilization of the quinoid form in the presence of a high density of defects. The smaller energy band gap for π - π^* transitions in the quinoid conformation relative to that for the benzenoid form allows for a resonance condition to be present for laser excitation wavelengths (λ_{exc}) near the visible (~1–2 eV). This results in a small dispersion effect in the observed quinoid breathing mode band which can be compared to dispersion effects previously reported for the case of *trans*-PA. The decrease in bandgap for the defect-induced quinoid form is also evidenced in the PL spectra of samples heat-treated up to 650 °C, which show vibronic structure in the blue-green emission data in the energy range 2.4–3.0 eV. Franck-Condon analysis shows an increase in the Huang-Rhys parameter (S) with increasing T_{HT} which can

be related to changes in the electron-phonon coupling of valence and conduction band states.

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Quantitative assessment of pores in oxidized carbon spheres using scanning tunneling microscopy

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Surface heterogeneity, particularly shape and size of pores on the surface, of activated carbon spheres were studied by using scanning tunneling microscopy (STM) and field-emission scanning tunneling microscopy (FE-SEM). Spheres were carbonized either in N₂ or CO₂ atmosphere and oxidized ones were used as samples. A new numerical method based on the determination of contour maps from STM images was proposed in order to determine the size distribution in micropores. These results were discussed with respect to the adsorption of gas and liquid molecules. A good correlation between Brunauer, Emmet, and Teller (BET) surface area determined from adsorption isotherms of N₂ at 77 K and the number of pores with the size of 0.5–1.8 nm was observed, indicating that the proposed procedure to analyze the pore size distribution is effective.

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Computer simulation of grain growth kinetics with solute-drag

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The effects of solute-drag on grain growth kinetics were studied in two-dimensional (2-D) computer simulations by using a diffuse-interface field model. It is shown that, in the low velocity/low driving force regime, the velocity of a grain boundary motion departs from a linear relation with driving force (curvature) with solute-drag. The nonlinear relation of migration velocity and driving force comes from the dependence of grain boundary energy and width on the curvature. The growth exponent m of power growth law for a polycrystalline system is affected by the segregation of solutes to grain boundaries. With the solute-drag, the growth exponent m can take any value between 2 and 3 depending on the ratio of lattice diffusion to grain boundary mobility. The grain size and topological distributions are unaffected by solute-drag, which are the same as those in a pure system.

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Resonant Raman study of polyparaphenylene-based carbons

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A resonant Raman study of polyparaphenylene (PPP) prepared by the Kovacic and the Yamamoto methods and heat-treated at temperatures T_{HT} between 650 and 750 °C has been performed using different laser excitation energies E_{laser} between 1.92 and 3.05 eV. For samples treated at low T_{HT} , the Raman spectra change with E_{laser} and this behavior is ascribed to the coexistence of two forms of the PPP polymer (benzenoid and quinoid) and of a disordered carbon material. For higher T_{HT} samples, only a dispersion of the position of the Raman band as a function of E_{laser} is observed and explained as due to the carbonization of the original polymer. The transition temperature between these two regions of resonance behavior is lower for the Yamamoto-PPP samples than for the Kovacic-PPP samples.

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Film microstructure–deposition condition relationships in the growth of epitaxial NiO films by metalorganic chemical vapor deposition on oxide and metal substrates

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High-quality epitaxial or highly textured NiO thin films can be grown at temperatures of 400–750 °C by low-pressure metalorganic chemical vapor deposition (MOCVD) on MgO, SrTiO₃, C-cut sapphire, as well as on single crystal and highly textured Ni (200) metal substrates using Ni(dpm)₂ (dpm = dipivaloylmethanate) as the volatile precursor and O₂ or H₂O as the oxidizer/protonolyzer. X-ray diffraction (XRD), Scanning electron microscopy/energy dispersive detection (SEM/EDX), and atomic force microscopy (AFM) confirm that the O₂-derived NiO films are smooth and that the quality of the epitaxy can be improved by decreasing the growth temperature and/or the precursor flow rate. However, low growth temperatures (400–500 °C) lead

to rougher surfaces and carbon contamination. The H₂O-derived NiO films, which can only be obtained at relatively high temperatures (650–750 °C), exhibit slightly broader ω scan full-width half-maximum (FWHM) values and rougher surfaces but no carbon contamination. Using H₂O as the oxidizer/protonolyzer, smooth and highly textured NiO (111) films can be grown on easily oxidized single-crystal and highly textured Ni (200) metal substrates, which is impossible when O₂ is the oxidizer. The textural quality of these films depends on the quality of the metal substrates and the gaseous precursor flow rate.

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Synthesis and characterization of B–C–N compounds on molybdenum

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B–C–N compounds were prepared on molybdenum by means of bias-assisted hot filament chemical vapor deposition (HFCVD). Effect of the substrate temperature (T_s) on the growth of B–C–N films has been investigated systematically by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) based on the detailed analysis and calculation of the XPS. The substrate temperature plays a key role in the formation of the bonding states, the composition, and the surface morphology. Boron carbonitride is the main phase at all depositing temperatures, and the obtained compounds are as follows: B_{0.83}C_{0.17} + B_{0.39}C_{0.35}N_{0.26} at 873 K, B_{0.30}C_{0.34}N_{0.36} at 973 K, B_{0.64}C_{0.36} + B_{0.51}C_{0.23}N_{0.26} at 1073 K, B_{0.51}C_{0.31}N_{0.18} at 1173 K, and B_{0.37}C_{0.54}N_{0.09} at 1273 K.

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Quantitative evaluation of adhesion of diamond coatings

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This paper presents a model to evaluate quantitatively the adhesion of diamond coating according to indentation tests. It is found that small indentation load causes round spallation of the coating, no matter what the shape of the indenter is. An exponential sink-in deformation of the coating under the indentation is proposed ($y = -a \exp(-bx)$). The deformation stress at the spallation edge is considered the coating adhesion. Using experimentally observed relation of the indentation load versus the film spallation radius, we evaluate the adhesion of a diamond coating on copper to be about 1.921–1.956 GPa, which is in agreement with thermal quench results. The validity of this model is also verified by its self-consistence.

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Diamond deposition on Ni/Ni-diamond coated stainless steel substrate

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Electrodeposited Ni and Ni-diamond composite layers were used as diffusion barrier for Fe to facilitate the diamond growth on stainless steel substrates. Raman spectroscopy and scanning electron microscopy show the formation of good quality diamond crystallites by chemical vapor deposition.

X-ray diffraction results indicate that the expansion of Ni unit cell has taken place due to the formation of the Ni–C solid solution. This observation is also well supported by x-ray photoelectron spectroscopy studies. The lattice constant of the expanded Ni unit cell matches closely with the diamond, and this may be helpful in explaining the epitaxial growth of diamond on single-crystal Ni observed by others.

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Growth of carbon nitride thin films by radio frequency-plasma-enhanced chemical vapor deposition at low temperatures

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In this paper, we report our findings in the deposition of carbon nitride by radio frequency-plasma-enhanced chemical vapor deposition (RF-PECVD) at temperatures slightly above room temperature (RT) and pressures of 800 mTorr using NH₃ and C₂H₄ as source gases. The variation of the NH₃/C₂H₄ source gas ratio and RF power is shown to affect the N/C ratio and sp³/sp² ratio in a reproducible manner. An N/C ratio as high as 1.17 has been obtained under optimized growth conditions of NH₃/C₂H₄ ratio of 7.3 and RF power of 90 W. X-ray diffraction (XRD) indicate the presence of microcrystalline carbon nitride in an amorphous CN_x matrix with preferred orientation along the (100) direction. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) studies show that our assignment of the XPS peaks and FTIR absorption bands are mutually consistent and in good agreement with published data. Both methods of analysis show the increase in the sp³ component with increase in N incorporation in the film.

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Inelastic neutron scattering study of the hydration of tricalcium silicate

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Inelastic neutron scattering is applied for the first time to monitor directly the concentration of calcium hydroxide formed during the hydration of tricalcium silicate. Results taken between 10 and 40 °C show that the onset of calcium hydroxide formation is delayed at lower temperatures but that the final quantity formed appears to be converging to a temperature-independent value. At 20 °C, the 28 day value is 1.3 moles per mole of tricalcium silicate. Combining these results with previous measurements of the free water index made using quasielastic neutron scattering reveals that the hydrogen content of the C–S–H gel decreases significantly at increased curing temperature.

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